

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup>:</b> A61L 15/00, C08F 2/32, 8/00	<b>A1</b>	<b>(11) International Publication Number:</b> WO 95/05856 <b>(43) International Publication Date:</b> 2 March 1995 (02.03.95)
<b>(21) International Application Number:</b> PCT/US94/09665 <b>(22) International Filing Date:</b> 26 August 1994 (26.08.94) <b>(30) Priority Data:</b> 9317867.1 27 August 1993 (27.08.93) GB <b>(71) Applicant (for all designated States except US):</b> THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> GARTNER, Herbert, Alfons [DE/DE]; Rebgasse 15, D-76534 Baden-Baden (DE). BURGERT, Josef, Hermann [DE/DE]; Am Eichberg 15, D-77855 Achem (DE). KÖSTEL, Claudia [DE/DE]; Grüner Winkel 19, D-77876 Kappelrodeck (DE). <b>(74) Agent:</b> ROBERTS, John, H.; The Dow Chemical Company, Patent Dept., P.O. Box 1967, Midland, MI 48641-1967 (US).		<b>(81) Designated States:</b> AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KE, KG, KR, KZ, LK, LT, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> AQUEOUS FLUID ABSORBENT POLYMERS HAVING A SUPERIOR BALANCE OF ABSORPTIVE PROPERTIES		
<b>(57) Abstract</b> <p>The subject invention pertains to an aqueous fluid absorbent polymer having a superior balance of absorptive properties. In particular, the subject invention provides an aqueous fluid absorbent polymer characterized by a centrifuge capacity of at least 25 grams/gram, and an absorption under a 1.0 psi (70,000 dynes/cm<sup>2</sup>) load of at least 15 grams/gram. The subject invention further provides a process for preparing such polymers, which process employs an inhibitor during heat-treatment of the polymer. The subject invention further provides an absorbent structure comprising a fiber matrix and an aqueous fluid absorbent polymer characterized by a centrifuge capacity of at least 25 grams/gram, and an absorption under a 1.0 psi (70,000 dynes/cm<sup>2</sup>) load of at least 15 grams/gram.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

AQUEOUS FLUID ABSORBENT POLYMERS HAVING A SUPERIOR  
BALANCE OF ABSORPTIVE PROPERTIES

The subject invention pertains to an aqueous fluid absorbent polymer having improved properties, to a process for the preparation of such a polymer, and to an absorbent structure incorporating such a polymer.

Aqueous fluid absorbent polymers (also known as superabsorbent polymers) are primarily used in personal care products which absorb bodily fluids, such as baby diapers, adult incontinence products, and feminine hygiene products. In such applications, aqueous fluid absorbent polymers are incorporated into absorbent structures which typically contain synthetic and/or natural fiber-based or paper-based woven and nonwoven structures, or toughened masses of fibers, such as fluff pads. The structures, in the absence of aqueous fluid absorbent polymers, have limited absorption capacity, are bulky due to the large amount of material needed to provide absorption capacity, and do not retain fluid well under pressure. The incorporation into the structures of aqueous fluid absorbent polymers, which imbibe fluids to form a swollen hydrogel material, serves to improve the absorption capacity and the absorption under pressure of the absorbent structure, to decrease the bulk by reducing (if not eliminating) the amount of fluff or fibers required, and to give the absorbent structure a "dry feel" even when wetted.

The performance of aqueous fluid absorbent polymers is typically measured by considering various properties, such as the capacity of the polymer, the ability of the polymer to absorb aqueous fluids under various pressures, the level of uncrosslinked extractable polymer present in the polymer, and the level of residual monomer present in the polymer. Ideally, industry would prefer a polymer which has a high capacity and a high absorption despite the application of moderate pressures. Industry would typically prefer that such a polymer further be characterized by low levels of extractable polymer, and low levels of residual monomer. However, achieving such a balance of properties has proved difficult.

An increased capacity typically results as the degree of crosslinking is decreased, that is, a looser polymer network is achieved. However, as the degree of crosslinking is decreased, the ability to absorb aqueous fluids under pressure typically decreases and the level of uncrosslinked extractable polymer typically increases. While advances have been made in terms of achieving a polymer having both a high capacity and a high absorption under relatively low pressures, for example, 0.3 psi (21,000 dynes/cm<sup>2</sup>) pressures, polymers having both a high capacity and a high absorption under higher pressures, for example, 1.0 psi (70,000 dynes/cm<sup>2</sup>) pressures, have remained elusive.

PCT Patent Application 92/07611 discloses a process for preparing an aqueous fluid absorbent polymer having improved absorptive properties wherein a dried aqueous fluid absorbent polymer is heat-treated at a temperature greater than 165°C in the absence of a

surface crosslinking agent to improve the 0.3 psi (21,000 dynes/cm<sup>2</sup>) AUL without significantly adversely affecting the centrifuge capacity. In a preferred embodiment, PCT Patent Application 92/07611 discloses that the heat-treatment of aqueous fluid absorbent polymers crosslinked with preferred crosslinking agents, such as methylenebisacrylamide, bis(acrylamido)acetic acid and its salts, allyl acrylate, allyl methacrylate, and other difunctional monovinyl and monoallyl esters and amides results in polymers having an increased centrifuge capacity and absorbency under load (AUL).

Great Britain Patent Application No. 9208449.0 discloses aqueous fluid absorbent polymers containing carboxyl moieties which are crosslinked using C<sub>2-10</sub> polyhydric hydrocarbons which are ethoxylated with from 2 to 8 ethylene oxide units per hydroxyl moiety of the ethylene oxide chain, wherein the hydroxy moiety at the end of each chain is esterified with a C<sub>2-10</sub> unsaturated carboxylic acid or ester thereof, one example of which is highly ethoxylated trimethylolpropane triacrylate. In a preferred embodiment, the aqueous fluid absorbent polymer is subjected to a heat-treatment after drying and sizing the particles. The utilization of such ethoxylated crosslinking agents, particularly as prepared by a process under which the polymer is heat-treated, results in aqueous fluid absorbent polymers which are characterized by a moderate centrifuged capacity in the range of 25 to 35 g/g, a 0.3 psi (21,000 dynes/cm<sup>2</sup>) AUL in the range of 25 to 31 g/g and a 1.0 psi (70,000 dynes/cm<sup>2</sup>) AUL in the range of 7 to 18 g/g. Within these ranges, products with high centrifuge capacities, for example, centrifuge capacities at the upper end of the range have been found to have 1.0 psi (70,000 dynes/cm<sup>2</sup>) AUL's at the lower end of the range, while products with high 1.0 psi (70,000 dynes/cm<sup>2</sup>) AUL's, for example, 1.0 psi (70,000 dynes/cm<sup>2</sup>) AUL's between 10 and 18 g/g have been found to have centrifuge capacities at the low end of the range. Heretofore, aqueous fluid absorbant polymers have not provided both high centrifuge capacity and high AUL.

The heat-treatment of aqueous fluid absorbent material crosslinked with preferred crosslinking agents, such as the crosslinking agents disclosed in PCT Patent Application 92/07611 and in Great Britain Patent Application No. 9208449.0, in and of itself may not permit the achievement of high capacity coupled with high absorption under relatively high pressure, for example, a centrifuge capacity greater than 25 grams/gram and a 1.0 psi (70,000 dynes/cm<sup>2</sup>) AUL greater than 15 grams/gram. While not wishing to be bound by theory, it is now believed that during heat-treatment, amongst other reactions, a chain scission reaction occurs, which is believed to result in a decrease in crosslink density. As crosslink density at the surface of the particles decreases, the potential for high absorption under relatively high pressure likewise decreases.

U.S. Patent No. 4,666,983 discloses an absorbent article obtained by mixing 100 parts by weight of an absorbent resin powder having a carboxyl group with 0.0001 to 10 parts by weight of a crosslinking agent to crosslink the molecular chains existing at least in the vicinity of the surface of the absorbent resin powder. U.S. Patent No. 4,734,478 discloses a

water-absorbing resin powder having the molecular chains near its surface crosslinked, the resin powder being obtained by mixing 100 parts by weight of a powder of a carboxyl-containing water-absorbing resin with 0.001 to 10 parts by weight of a polyhydric alcohol and heating the mixture at a temperature of at least 100°C to react the powder with the polyhydric alcohol, the improvement comprising conducting the mixing of the powder and the polyhydric alcohol in the presence of 0.01 to 8 parts by weight of a hydrophilic organic solvent and 0 to 8 parts by weight of water per 100 parts by weight of the powder. Such surface crosslinking agents function by chemically reacting with the polymer at its surface, at elevated temperatures, to further crosslink the polymer at the surface. Such surface crosslinking agents do not inhibit chain scission at high temperatures. Thus, while the use of surface crosslinking agents may somewhat compensate for the effect of chain scission, they do not minimize or prevent it.

Industry would find great advantage in an aqueous fluid absorbent polymer which exhibits a high capacity and a high absorption under a moderately high pressure. Industry would further find great advantage in an aqueous fluid absorbent polymer which not only exhibits a high capacity and a high absorption under a moderately high pressure, but which further exhibits a low level of extractable polymer and/or a low level of residual monomer. Industry would further find great advantage in a process for preparing such polymers, which process has the flexibility of optimizing polymer performance with respect to the above-identified properties, and in absorbent structures which incorporate any of such aqueous fluid absorbent polymers.

Accordingly, the subject invention provides an aqueous fluid absorbent polymer comprising the polymerization product of an ethylenically unsaturated monomer and optionally a comonomer copolymerizable with the ethylenically unsaturated monomer, the aqueous fluid absorbent polymer being crosslinked by a crosslinking agent having at least two moieties which react with the ethylenically unsaturated monomer and optionally the comonomer, wherein the aqueous fluid absorbent polymer is characterized by a centrifuge capacity of at least 25 grams/gram, and an absorption under a 1.0 psi (70,000 dynes/cm<sup>2</sup>) load of at least 15 grams/gram. It is preferable that the polymer have a centrifuge capacity of 28, 30 or even 33 grams/gram. More preferable is a centrifuge capacity of 35 grams/gram or more. It is preferable that the polymer has an absorption under load of 1.0 psi of 18, 20 or even 21 grams/gram. More preferable is an absorption under load of 1.0 psi of 23, 24 or more grams/gram.

The subject invention further provides such an aqueous fluid absorbent polymer wherein the level of extractable polymer is less than 18 preferably less than 15, more preferably less than 12 percent. Extractable levels less than 10 percent can be observed.

The subject invention further provides a process for preparing an aqueous fluid absorbent polymer comprising:

- (a) polymerizing an ethylenically unsaturated monomer and optional comonomer copolymerizable with the ethylenically unsaturated monomer, in the presence of a crosslinking agent having at least two moieties which react with the ethylenically unsaturated monomer and optionally the comonomer, to form aqueous fluid absorbent beads or a hydrogel;
- (b) removing solvent from the aqueous fluid absorbent beads or water from the hydrogel to form a dried aqueous fluid absorbent polymer material; and
- (c) heat treating the dried aqueous fluid absorbent polymer material at a temperature from 170°C to 240°C to form a heat-treated aqueous fluid absorbent polymer material;
- wherein the dried aqueous fluid absorbent polymer material contains an inhibitor during the heat-treating of step (c), the inhibitor being provided subsequent to the polymerizing of step (a) and prior to the heat-treating of step (c).

The subject invention further provides an absorbent structure comprising a fiber matrix and an aqueous fluid absorbent material characterized by a centrifuge capacity of at least 25 grams/gram, and an absorption under a 1.0 psi (70,000 dynes/cm<sup>2</sup>) load of at least 16 grams/gram.

#### Detailed Description

As described in U.S. Patent Application Serial No. 756,731, Great Britain Patent Application No. 9208449.0, and PCT Application 92/07611, post-drying heat-treatment of aqueous fluid absorbent polymers improves the balance of absorptive properties, as between the 0.3 psi (21,000 dynes/cm<sup>2</sup>) absorption under load and the centrifuge capacity. However, while not wishing to be bound by theory, it is believed that heat-treatment promotes a competing radical reaction, which causes chain scission by the influence of oxygen, and a resultant decrease in crosslink density. Through the practice of the subject invention, an inhibitor is added to the dry polymer, typically as an aqueous or aqueous/organic solution, prior to heat-treatment. It is believed that the presence of the inhibitor minimizes or suppresses the undesired radical reaction by trapping the radicals formed by heat-treatment before chain scission occurs. Regardless of the mechanism involved, the inventive polymers possess a superior balance of absorptive properties.

The aqueous fluid absorbent polymer of the invention is derived from one or more ethylenically unsaturated monomers, such as ethylenically unsaturated carboxylic acids, ethylenically unsaturated carboxylic acid anhydrides or salts thereof. Preferably ethylenically unsaturated carboxylic acid and carboxylic acid anhydride monomers include the acrylic acids typified by acrylic acid, methacrylic acid, ethacrylic acid,  $\alpha$ -chloroacrylic acid,  $\alpha$ -cyanoacrylic acid,  $\beta$ -methacrylic acid (crotonic acid), isocrotonic acid,

$\alpha$ -phenylacrylic acid,  $\beta$ -acryloyloxypropionic acid, sorbic acid,  $\alpha$ -chlorosorbic acid, angelic acid, cinnamic acid, p-chlorocinnamic acid,  $\beta$ -styrylacrylic acid (1-carboxy-4-phenyl butadiene-1,3), itaconic acid, citraconic acid, mesaconic acid, glutaconic acid, maleic acid, fumaric acid and maleic acid anhydride. More preferably the ethylenically unsaturated monomer is acrylic acid, methacrylic acid, or a salt thereof, with acrylic acid or a salt thereof being most preferred.

Additionally, the aqueous fluid absorbent polymer may include one or more comonomers known in the art for use in aqueous fluid absorbent polymers or for grafting onto the ethylenically unsaturated monomers or other comonomers such as an acrylamide, a methacrylamide, 2-acrylamido-2-methyl-1 propane sulfonic acid, an acrylonitrile, a vinyl pyrrolidone, a vinyl sulphonic acid, a cellulosic monomer, a modified cellulosic monomer, a polyvinyl alcohol, a starch hydrolyzate, and salts thereof. When grafting polymers, such as polyvinyl alcohols, are employed, they are typically provided in amounts up to about 30 weight percent, more typically up to about 10 weight percent, based on the weight of the ethylenically unsaturated monomer.

Among preferred aqueous fluid absorbent polymers are hydrolyzates of starch-acrylonitrile graft copolymers, partially neutralized products of starch-acrylic acid graft copolymers, saponification products of vinyl acetate acrylic ester copolymers, hydrolyzates of acrylonitrile copolymers, crosslinked products of hydrolyzates of acrylonitrile copolymers, hydrolyzates of acrylamide copolymers, crosslinked products of hydrolyzates of acrylamide copolymers, partially neutralized products of polyacrylic acids and crosslinked products of partially neutralized polyacrylic acids.

The aqueous fluid absorbent polymer will preferably be lightly crosslinked to render it water-insoluble. The desired crosslinked structure may be obtained by the copolymerization of the selected ethylenically unsaturated monomer and optional comonomer with a crosslinking agent possessing at least two polymerizable double bonds in the molecular unit. The crosslinking agent is present in an amount effective to crosslink the water-soluble polymer. The preferred amount of crosslinking agent is determined by the desired degree of absorption capacity and the desired strength to retain the absorbed fluid, that is, the desired absorption under load (AUL). Typically, the crosslinking agent is used in amounts ranging from 0.0005 to 1.5 parts by weight per 100 parts by weight of the ethylenically unsaturated monomer used. More preferably, the amount ranges from 0.1 to 1.5 parts by weight per 100 parts by weight of the ethylenically unsaturated monomer. If an amount over about 5 parts by weight of crosslinking agent per 100 parts is used, the resulting polymer has too high a crosslinking density and exhibits a reduced absorption capacity and increased strength to retain the absorbed fluid. If the crosslinking agent is used in an amount less than about 0.0005 part by weight per 100 parts, the polymer has too low a crosslinking density, and when contacted with the fluid to be absorbed becomes sticky and exhibits a lower initial absorption rate.

While the crosslinking agent will typically be soluble in the aqueous monomer solution, the crosslinking agent may be merely dispersible in such a solution, without negative implications. The use of such dispersing agents is disclosed in U.S. Patent No. 4,833,222.

Suitable dispersing agents include carboxymethyl cellulose suspending aids, methyl cellulose, hydroxypropyl cellulose, and polyvinyl alcohol. Such dispersing agents are typically provided at a concentration between 0.005 and 0.1 weight percent, based on the total weight of ethylenically unsaturated monomer.

Typical crosslinking agents include compounds having at least two polymerizable double bonds; compounds having at least one polymerizable double bond and at least one functional group reactive with the monomers and one functional group reacting with the monomers or functional group of a monomer unit in the polymer; and compounds having at least two functional groups reactive with the ethylenically unsaturated monomer. Preferred crosslinking agents include compounds having in one molecule 2 to 4 groups such as  $\text{CH}_2 = \text{CHCO}-$ ,  $\text{CH}_2 = \text{C}(\text{CH}_3)\text{CO}-$  or  $\text{CH}_2 = \text{CH}-\text{CH}_2-$ . Additional preferred crosslinking agent include polyvalent metal compounds which can form ionic crosslinkages.

Exemplary compounds having at least two polymerizable double bonds include divinyl or polyvinyl compounds such as divinylbenzene, divinyl toluene, divinyl xylene, divinyl ether, divinyl ketone and trivinylbenzene; diesters or polyesters of unsaturated monocarboxylic acids or polycarboxylic acids with polyols, such as dimethacrylic acid or trimethacrylic acid esters of polyols, such as ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, tetrapropylene glycol, trimethylolpropane, glycerine, polyoxyethylene glycols, polyoxypropylene glycols; unsaturated polyesters that can be obtained by reacting any of the above-mentioned polyols with an unsaturated acid such as maleic acid; and dimethacrylic acid or trimethacrylic acid esters that can be obtained by reacting polyepoxide with methacrylic acid; bismethacrylamides such as N,N'-methylenebisacrylamide; carbamyl esters that can be obtained by reacting polyisocyanates such as tolylene diisocyanate, hexamethylene diisocyanate, 4,4'-diphenyl methane diisocyanate and NCO-containing prepolymers that can be obtained by reacting such isocyanates with active hydrogen atom-containing compounds with hydroxyl group-containing monomers, such as dimethacrylic acid carbamyl esters obtainable by reacting the above-mentioned diisocyanates with hydroxyethylmethacrylate; dimethallyl or polymethallyl ethers of polyols such as alkylene glycols, glycerol, polyalkylene glycols, polyoxyalkylene polyols, and carbohydrates, such as polyethylene glycol diallyl ether, allylated starch, and allylated cellulose; diallylesters or polyallylesters of polycarboxylic acids, such as diallylphthalate and diallyladipate; and esters of unsaturated monocarboxylic or polycarboxylic acids with monomethallyl esters of polyols, such as the methacrylic acid ester of polyethylene glycol monoallyl ether.



Preferable compounds having at least one polymerizable double bond and at least one functional group reactive with the monomers include ethylenically unsaturated compounds containing at least one group reactive with carboxyl, carboxylic acid anhydride, hydroxyl, amino or amide groups. Such compounds include N-methylolmethacrylamide and glycidylmethacrylate.

Preferable compounds having at least two functional groups reactive with the monomers include difunctional or polyfunctional compounds which contain groups reactive with carboxyl, carboxylic acid anhydride, hydroxyl, amino or amide groups. Examples are glyoxal; polycarboxylic acids, such as phthalic acid, and adipic acid; polyols, such as described hereinbefore; polyamines, such as alkylene diamines (for example, ethylenediamine) and polyalkylenepolyamines.

Preferable polyvalent metal compounds which can form ionic crosslinkages include oxides, hydroxides, and weak acid salts, for example, carbonate and acetate salts, of alkaline earth metals.

As noted in PCT Application 92/07611, a certain class of crosslinking agents yields particularly preferred absorptive properties. Such preferred crosslinking agents include methylenebisacrylamide, bis(acrylamido)acetic acid and its salts, allyl acrylate, allyl methacrylate, and esters or amides having both a vinyl and an allyl functionality.

As noted in Great Britain Patent Application No. 9208449.0, other preferred crosslinking agents include C<sub>2-10</sub> polyhydric hydrocarbons which are ethoxylated with from 2 to 8 ethylene oxide units per hydroxyl moiety of the ethylene oxide chain wherein the hydroxy moiety at the end of each chain is esterified with a C<sub>2-10</sub> unsaturated carboxylic acid or ester thereof, one example of which is trimethylol propane which has been ethoxylated with 2 to 7 ethylene oxide units per hydroxy moiety and wherein each hydroxy moiety has been esterified with an acrylate moiety. Such preferred crosslinking agents are known as highly ethoxylated trimethylolpropane triacrylate.

Especially preferred crosslinking agents are diacrylates and dimethacrylates of ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, trimethylolpropane and pentaerythritol; triacrylates and trimethacrylates of trimethylolpropane and pentaerythritol; highly ethoxylated trimethylolpropane triacrylate and trimethacrylate; highly ethoxylated pentaerythritol tri(meth)acrylate, tetraacrylate and tetra(meth)acrylate of pentaerythritol; highly ethoxylated pentaerythritol tetra(meth)acrylate; tetraacrylate and tetramethacrylate of pentaerythritol; tetraallyloxyethane; methylenebisacrylamide; bis(acrylamido)acetic acid and its salts; allyl acrylate; allyl methacrylate; and esters or amides having both a vinyl and an allyl functionality. The more preferred class of crosslinkers are allyl methacrylates, the diallyl or polyallyl esters of polycarboxylic acids, and highly ethoxylated trimethylolpropane triacrylate.

In a gel polymerization process, the ethylenically unsaturated monomers, optional comonomers, and crosslinking agent are preferably dissolved, dispersed, or suspended in an aqueous medium in an amount ranging from 10 percent to 80 percent by weight based on the total weight of the aqueous monomer solution, to form a reaction mixture. Preferably, the amount ranges from 20 percent to 60 percent based on the total weight of the aqueous monomer solution.

Other components may be provided in the aqueous reaction mixture. For instance, it may be advantageous to include a chelating agent to remove trace metals from solution, for example, when a metal reaction vessel is employed. One such chelating agent is VERSENEX™ V-80 (an aqueous solution of the pentasodium salt of diethylenetriamine pentaacetic acid) (Trademark of The Dow Chemical Company). Such chelating agents, when employed, are generally used in amounts between 100 and 2000 ppm based on the weight of the ethylenically unsaturated monomer.

Conveniently, a conventional vinyl addition polymerization initiator is included in the reaction mixture. A free radical polymerization initiator which is sufficiently soluble in the reaction mixture to initiate polymerization is preferred. For example, water-soluble peroxygen compounds are preferred. Exemplary water-soluble peroxygen compounds include water-soluble persulfates such as ammonium persulfate, potassium persulfate, sodium persulfate, other alkali-metal persulfates, hydrogen peroxide, caprylyl peroxide, benzoyl peroxide, cumene hydroperoxides, tertiary butyl perbenzoate, sodium peracetate, sodium percarbonate hydroperoxides, and water-soluble azo-compounds such as 2,2'-azobis (2-amidinopropane·HCl). Conventional redox initiator systems can also be utilized, which are formed by combining the foregoing peroxygen compounds with reducing agents such as sodium bisulfite, sodium thiosulphate, ascorbic acid or a salt thereof, or ferrous salts. The initiator can comprise up to about 5 mole percent based on the total moles of ethylenically unsaturated monomer and optional comonomer present. More preferably the initiator comprises from 0.001 to 0.5 mole percent based on the total moles of ethylenically unsaturated monomer and optional comonomer present in the reaction mixture.

It is desirable to obtain a level of conversion of monomer to polymer of at least about 95 percent. The polymerization may be carried out using acid monomers that are not neutralized or that have been neutralized or partially neutralized prior to the polymerization. Neutralization is conveniently achieved by contacting the aqueous monomer with an amount of basic material sufficient to neutralize between 20 and 95 percent of the acid groups present in the acid monomers. Preferably, the amount of basic material will be sufficient to neutralize between 40 percent and 85 percent, and most preferably between 55 percent and 75 percent of the acid groups present in the acid monomers. When pre-neutralizing the monomer solution, it is important to control the neutralization conditions so that the heat of neutralization does not cause the premature polymerization of the monomer mixture. The

neutralization is advantageously carried out at temperatures below about 40°C, preferably at temperatures below about 35°C.

Compounds which are useful to neutralize the acid groups of the monomer are typically those which will sufficiently neutralize the acid groups without having a detrimental effect on the polymerization process. Such compounds include alkali metal hydroxides, and alkali metal carbonates and bicarbonates. Preferably, the material used to neutralize the monomer is sodium or potassium hydroxide or sodium carbonate or potassium carbonate. In determining the desired degree of neutralization, care must be taken to ensure that the pH of the resulting crosslinked absorbent polymer, which will be contacted with or dispersed in an aqueous fluid to be absorbed, is maintained in a range appropriate for the applications for which the polymer is intended. Alternatively, the polymerization may be carried out employing unneutralized monomers and thereafter neutralizing, as is known in the art.

In a preferred embodiment for making polymers useful in the practice of this invention, an aqueous solution of the ethylenically unsaturated monomer in the partially neutralized form, the optional comonomer, the crosslinking agent, and the initiator is prepared. The polymerization of the mixture may be initiated by elevating the temperature of the mixture containing the initiator or by using a redox-type initiator as described above. Typically, the reaction is performed under an inert gas atmosphere, for example under nitrogen or argon, in order to remove and separate oxygen from the monomer mixture to allow proper initiation of the polymerization.

Generally, the temperature at which polymerization will begin ranges from 20°C to 45°C. The precise temperature at which the polymerization is carried out will be selected in view of the type and concentration of the monomers, the initiator types and concentrations, and the type and size of the polymerization reactor. Preferably, the maximum temperature of polymerization ranges from 50°C to 100°C, more preferably from 60°C to 90°C, and most preferably from 70°C to 85°C. As the reaction is exothermic, it may be desirable to provide a means for cooling the reactor so as to maintain a desired temperature. The method by which the temperature of the polymerization is controlled is not critical so long as sufficient cooling is present to remove the heat which is generated during the polymerization.

The reaction mixture will be reacted for a time sufficient to result in the desired conversion of monomer to crosslinked hydrogel. Preferably, the conversion is 95 percent or greater, more preferably 98 percent or greater, and most preferably 99 percent or greater. To achieve such levels of conversion, the reaction time will typically be at least 20 minutes, more typically at least 40 minutes, and most typically at least 1 hour. For largely economic reasons, the reaction time will preferably be no more than 6 hours, more preferably no more than 4 hours, and most preferably no more than 3 hours.

During polymerization, the resultant crosslinked polymer generally absorbs all of the aqueous reaction medium to form a hydrogel. The term hydrogel, as used herein, refers to

water swollen aqueous fluid absorbent polymer having a water content of at least about 10 weight percent, more typically at least about 15 weight percent, based on the weight of the hydrogel. In embodiments wherein the hydrogel is dried by means other than the hot air present in the reactor during the exothermic polymerization, the water content of the hydrogel upon completion of the polymerization reaction will typically be in the range of 50 to 80 weight percent.

The resultant hydrogel is typically pre-sized and dried using means well-known in the art. The size of the gel particles after pre-sizing should be such that homogeneous drying of the particles can occur. Pre-sizing can be performed by any means known in the art which gives the desired result. Typically, the pre-sizing is performed by chopping the hydrogel. In one embodiment, the resultant hydrogel is pre-sized by forcing it through a die such as is described in European Patent Application 497,623. When a through-circulation band dryer is employed, the obtained hydrogel granules will be distributed onto a conveyor belt leading to the dryer.

In some instances, drying will occur in two or more stages. In two-stage drying, the sized hydrogel particles are partially dried in the first stage, for example, the sized hydrogel particles are dried to less than about 10 percent moisture level, preferably about a 5 percent moisture level. During the initial drying, the hydrogel particles tend to fuse together to form a sheet. In two-stage driers, the partially dried hydrogel sheets may be broken to form pieces which are very roughly about 10 cm x 10 cm x 2 cm in dimension. Such pieces may then be more fully dried in the second stage, for example, dried to a moisture level less than about 7 percent. Following the completion of drying, the pieces are typically more fully sized to form particles having an average diameter less than about 0.8 mm.

The temperature at which the drying takes place is a temperature high enough such that the water and any optional organic solvent is removed in a reasonable time period and in an economically feasible fashion. Preferably, the temperature of the water-absorbent resin particles during drying is about 180°C or less. More preferably, the temperature during drying is from 100°C to 170°C, most preferably from 150°C to 170°C.

The drying time should be sufficient to remove the desired amount of water in a reasonable time period, and will depend on the drying system employed. Typically, the drying will reduce the moisture level of the hydrogel to a level from 1 to 5 weight percent. The drying time will be a function of the drying equipment, the size of the pre-sized hydrogel, and the operating conditions of the drying equipment. For economic reasons, the drying time will typically be no longer than necessary. Typically, the minimum time for drying is 10 minutes or greater, with 15 minutes or greater being preferred. Preferably, the drying time is 60 minutes or less, with 25 minutes or less being more preferred.

The dried aqueous fluid absorbent polymer will preferably be subjected to mechanical particle reduction means, for example, chopping, cutting, and/or grinding. Such

mechanical particle reduction means serve to reduce the particle size of the water-absorbent resin particles to a particle size acceptable in the ultimate end use. In a preferred mode, the aqueous fluid absorbent polymer is sized by first chopping, and then grinding. In a preferred embodiment, the resultant average particle size is less than about 2 mm, and is more preferably less than about 0.8 mm. Preferably, the resultant average particle size is at least about 0.04 mm, more preferably at least about 0.07 mm, and most preferably at least about 0.1 mm.

To improve absorptive properties, the dried particles may be heat-treated in accordance with the procedures set forth in PCT Application 92/07611. In particular, the dried particles are heated for a time sufficient to increase the absorbency under load. Such heat-treatment is preferably carried out at a temperature of at least about 170°C, more preferably of at least 190°C, most preferably at least 220°C. To avoid damage of the final product, such heat-treatment is preferably carried out at a temperature of less than about 250°C, more preferably less than about 240°C.

In the practice of the process of the subject invention, an inhibitor is present during heat-treatment. As used herein, the term "inhibitor," means a substance which scavenges radicals and therefore prevents polymer chain scission reactions or autooxidation reaction which occur in the presence of radicals and oxygen, or a substance which reduces intermediately formed hydroperoxide groups on the polymer before they cause chain cleavage. Inhibitors are generally well known in the art. A list by tradename of commercially available inhibitors is set forth in the Kirk and Othmer Encyclopedia of Chemistry, Volume 3, pages 128-148.

Antioxidants are a subset under the term "inhibitors." Antioxidants are useful to the extent that they prevent the autooxidation reaction between radicals on the polymer site and oxygen which would cause chain cleavage. Antioxidants are also useful to the extent that they are reducing agents which reduce intermediately formed polymer peroxides, as they are formed in the autooxidation process, before they cause chain cleavage. A list of typical antioxidants is contained in the article "Antioxidants," by Peter P. Klemchuk, Ciba-Geigy Corporation and published in Ullmann's Encyclopedia of Industrial Chemistry, Volume 3, page 91 ff, VCH-Verlagsgesellschaft D-6940 Weinheim (FRG). 5., completely revised edition 1985.

Exemplary inhibitors include hindered phenols, aromatic amines, sulfur compounds, phosphorus compounds or hindered amines, ascorbic acid and its derivatives, gallic acid and its derivatives, benzothiazoles, dithionates, thiurams, benzimidazoles, formaldehyde sulfoxylates and phenothiazines.

Specific examples of inhibitors particularly include ascorbic acid and its derivatives such as L-ascorbic acid, sodium L-ascorbate, isoascorbic acid, sodium isoascorbate; gallic acid and its derivatives such as gallic acid, methyl gallate, ethyl gallate, n-propyl gallate, isoamyl gallate, octyl gallate, lauryl gallate, pyrogallol; benzothiazoles such as mercaptobenzothiazole, sodium mercaptobenzothiazole, zinc mercaptobenzothiazole; dithionates such as zinc

methyldithiocarbamate, zinc diethyldithiocarbamate, zinc di-n-butyldithiocarbamate, zinc ethylphenyldithiocarbamate; thiurams such as tetramethylthiuram disulfide, tetraethylthiuram sulfide, tetrabutylthiuram disulfide, tetramethylthiuram monosulfide; benzimidazoles such as 2-mercaptobenzimidazole; formaldehyde sulfoxylates such as sodium formaldehyde sulfoxylate; and phenothiazines such as phenothiazine, 2-methoxyphenothiazine

Other inhibitors include sulfites as salts or acids, hydroquinone, p-methoxyphenol, benzoquinone, methyl hydroquinone, methoxyhydroquinone, t-butylhydroquinone, lignin sulfonate, flavonoids such as quercetin and ellagic acid and salts thereof, phenol compounds such as catechol, resorcinol and derivatives thereof, and amine compounds such as N-nitrosophenyl hydroxylamine ammonium salt, thiourea, tannic acid and salts thereof such as hydrolyzed-type tannin obtained from gall and condensed-type tannin obtained from gambier, citric acid, 1,1-bis(4-hydroxyphenyl)-cyclohexane,  $\beta$ -naphthol, 2,6-di-t-butyl-p-cresol, butylated hydroxyanisol, thiourea dioxide, dilauryl thiodipropionate, and triphenyl phosphite.

Such inhibitors may be used alone or in combination. Given the possibility of utility in personal care applications, preferred inhibitors may correspond to those useful as stabilizers for food, such as butylated hydroxytoluene, butylated hydroxyanisol, 2- and 3-tert-butyl-4-methoxyphenol, or 3,4,5-trihydroxybenzoic acid propyl ester (GAPE). In view of their exemplary performance, especially preferred inhibitors include gallic acid derivatives, such as GAPE.

The inhibitor will be provided prior to or during heat-treatment of the dried polymer. In one embodiment, the inhibitor will be applied to the polymer, subsequent to drying and prior to heat-treatment. In this embodiment, the inhibitor may be applied in one of at least two manners. In one manner in which the inhibitor is "substantially homogeneously present" in the aqueous fluid absorbent polymer, the inhibitor will be dissolved in water to form a solution, which solution is injected into a horizontal blender which contains the dry polymer. In this manner, the inhibitor solution and polymer are mixed for a time sufficient to permit the inhibitor solution to reach into the interior of the polymer particles. A more detailed description of this manner follows in the examples below, under the subheading "Inhibitor Addition and Distribution Procedure 1."

In another manner in which the inhibitor is "more highly concentrated at the particle surfaces" of the aqueous fluid absorbent polymer, the inhibitor will be dissolved in water and an optional organic solvent, such as isopropanol, to form a solution, which solution is added to the polymer particles. The solution may further contain a surfactant to facilitate distribution of the inhibitor on the surface of the polymer particles. The polymer particles/inhibitor solution composition is roll-mixed for a time sufficient to permit the inhibitor solution to contact the surface of the polymer particles, without substantially

penetrating the interior of the particles. A more detailed description of this manner follows in the examples below, under the subheadings "Inhibitor Addition and Distribution Procedure 2" (where no surfactant is employed) and "Inhibitor Addition and Distribution Procedure 3" (where a polyoxyethylene-(2)-sorbitol lanoline derivative is employed as a surfactant).

5 In another embodiment, the inhibitor will be applied to the hydrogel, subsequent to polymerization and prior to or during drying. In this embodiment, the inhibitor will be dissolved in water and an optional organic solvent, such as isopropanol, to form a solution, which the solution is then added to the hydrogel. At the time of addition of the inhibitor, the hydrogel will preferably be at a temperature greater than ambient temperature. Typical  
10 hydrogel temperatures are between 30°C. and 60°C. The inhibitor solution may further contain a surfactant to facilitate distribution of the inhibitor on the surface of the hydrogel granules. The hydrogel, as treated with the inhibitor solution, is thereafter dried and heat-treated. A more detailed description of this manner follows in the examples below, under the subheading "Inhibitor Addition and Distribution Procedure 4.

15 When the inhibitor is to be concentrated at the surface of the polymer particles, the inhibitor will preferably be provided in an amount of at least about 5 ppmw, more preferably at least about 25 ppmw, most preferably at least about 50 ppmw, based on the weight of the polymer particles. Likewise, the inhibitor will preferably be provided in an amount no greater than about 8000 ppmw, more preferably no greater than about 5000  
20 ppmw, more preferably no greater than about 2000 ppmw, most preferably no greater than about 500 ppmw, based on the weight of the polymer particles.

When the inhibitor is to be more homogeneously present in the polymer particles during heat-treatment, the inhibitor will preferably be provided in an amount of at least about 50 ppmw, more preferably about 100 ppmw, based on the weight of the polymer particles.  
25 Likewise, the inhibitor will preferably be provided in an amount no greater than about 5,000 ppmw, more preferably no greater than about 3,000 ppmw, most preferably no greater than about 2,000 ppmw, based on the weight of the polymer particles.

When the inhibitor is to be applied to the hydrogel, subsequent to polymerization and prior to or during drying, the inhibitor will preferably be provided in an  
30 amount of at least about 1000 ppmw, more preferably about 2000 ppmw, based on the weight of the hydrogel. Likewise, the inhibitor will preferably be provided in an amount no greater than about 10,000 ppmw, more preferably no greater than about 8,000 ppmw.

While it is not believed necessary to the performance of the polymer, the polymer of the invention may contain residual inhibitor, that is unreacted or partially reacted inhibitor.  
35 The level of residual inhibitor may be determined by extracting it with a hydrophylic solvent such as water and methanol an aliquot is then prepared for examination by UV spectroscopy. Typically, the aqueous fluid absorbent polymers of the invention will have a level of residual inhibitor equal to approximately half the amount of inhibitor added to the polymer. In view of

the recommended levels of inhibitor, the anticipated levels of residual inhibitor in the inventive polymers will typically be from 10 to 5000 ppmw, based on the weight of the aqueous fluid absorbent.

To facilitate uniform distribution, the inhibitor will preferably be applied as a liquid. When the inhibitor is a solid, it will typically be dissolved in a suitable solvent, such as water or a water/organic mixture. Typical organic solvents include low alcohols such as, methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, and t-butanol; ketones such as acetone, methylethyl ketone, and methylisobutyl ketone; ethers such as diethylether, diisopropylether, dipropylether, dibutylether, ethylisopropyl ether; cyclic ethers such as dioxane and tetrahydrofuran; amides such as N,N-dimethylformamide; and sulfoxides such as dimethylsulfoxide. To permit dissolution of the inhibitor, the solvent may be heated to the extent necessary.

Further, the inhibitor solution may optionally contain a surfactant. Typical surfactants are nonionic surfactants having an HLB value in the range of from 3 to 10 and which are dispersible in water. Preferable surfactants include sorbitan fatty acid esters, polyoxyethylene sorbitan fatty acid esters, glycerol or polyglycerol fatty acid esters, polyoxyethylene alkyl ethers, polyoxyethylene alkylphenol esters, polyoxyethylene acryl esters and sucrose fatty acid esters or modified surface active polyesters. More preferred surfactants are polyethoxylated sorbitol lanolin derivatives, for example a polyoxyethylene-(2)-sorbitol lanoline derivative available from ICI Specialty Chemicals (United Kingdom) under the Tradename G1425. When utilized, the surfactant will typically be present in the solution in an amount from 0.01 to 2 parts, more preferably from 0.075 to 0.5 parts, per hundred parts by weight of aqueous fluid absorbent resin.

Optionally, to the extent its presence does not hinder the formation of the inventive polymers having a centrifuge capacity of at least 25 g/g and a 1.0 psi (70,000 dynes/cm<sup>2</sup>) AUL of at least 15 g/g, chloric acid, bromic acid or a salt thereof may be present during the heat-treatment process. For instance, chloric acid, bromic acid, or a salt thereof is usefully added when the aqueous fluid absorbent polymer has been crosslinked with highly ethoxylated trimethylol propane triacrylate.

The counterion on the bromate or chlorate salt can be any counterion which does not significantly interfere in the preparation of the resin particles or their performance. Preferred counterions include alkaline earth metal ions or alkali metal ions. More preferred counterions include the alkali metals, with potassium and sodium being even more preferred. The chloric acid or salts thereof are most preferred.

When the chloric acid, bromic acid, or salt thereof is added directly to the reaction mixture, it is preferably provided in an amount of at least about 10 ppm, more preferably at least about 50 ppm, even more preferably at least about 100 ppm, and most preferably at least about 200 ppm by weight based on the total weight of the ethylenically unsaturated monomer



and optional comonomer present. When the chloric acid, bromic acid, or salt thereof is added directly to the reaction mixture, it is preferably provided in an amount less than about 1000 ppm, more preferably less than about 600 ppm, and most preferably less than about 500 ppm based on the total weight of the ethylenically unsaturated monomer and optional comonomer present.

The temperature of and time period for heat-treatment should be sufficient to effect an improvement in absorptive properties. The exact temperatures and times for heat-treatment will be affected by the equipment chosen, and can be determined empirically by examination of product properties. The resin particles are heated to the desired post-heat temperature and are maintained at such temperature until the 1.0 psi (70,000 dynes/cm<sup>2</sup>) AUL increases to at least 15 g/g. Preferably, the temperature of heat-treatment will be at least 180°C, more preferably at least 200°C, and most preferably at least 220°C. To avoid damage to the polymer, the temperature of heat-treatment will preferably be less than 250°C.

The resin particles are typically maintained at the desired temperature for 1 minute or more, preferably for 5 minutes or more. If the treatment time is too long, it becomes uneconomical and a risk is run that the resin particles may be damaged. Typically, resin particles are maintained at the desired temperature for 60 minutes or less, preferably 40 minutes or less, more preferably 30 minutes or less.

Heat-treatment can be accomplished by means known in the art. For example, forced air ovens, fluidized bed heaters and heated screw conveyors may be successfully employed. If desired, the heated polymer may be remoisturized for ease in handling. In a preferred embodiment, the heat-treated particles are contacted with water vapor, such as in a fluidized bed. The dry particles are contacted with a sufficient amount of water to reduce or eliminate the effects of the static electricity, yet not so much as to cause the particles to agglomerate. Preferably, the dry particles are humidified with 0.3 percent or more by weight of water and more preferably 1 percent or more by weight of water. Preferably, the dry particles are humidified with 10 percent or less by weight of water and more preferably 6 percent or less by weight of water.

Optionally, agglomeration prevention additives may be added to the crosslinked hydrophilic resin. Such additives are well known in the art and include inert inorganic particles such as silica, see for example U.S. Patent Nos 4,500,670, 4,286,082, 4,734,478, and German Patent No. 2,706,135.

To reduce the levels of unassociated dust, for example, unassociated aqueous fluid absorbent polymer particles having an average particle size less than 10 microns, which unassociated dust is often formed during final sizing of the polymer product, and/or to inhibit the formation of unassociated dust upon handling of the polymer, a dedusting agent may be mixed with the heat-treated product. The use of such a dedusting agent is set forth in PCT Patent Application 93/02872. As set forth herein, exemplary dedusting agents include water-

soluble, lower aliphatic polyols of greater than about 200 average molecular weight or lower polyalkylene glycols of 400 to 6000 average molecular weight. One preferred dedusting agent is a propylene oxide adduct of glycerol or a polyethylene glycol having an average molecular weight of 500 to 2000. In particular, exemplary dedusting agents include VORANOL™  
5 polyether polyols such as VORANOL™ 2070, VORANOL™ 2100, and VORANOL™ 3100 polyether polyols (all available from The Dow Chemical Company); polyethylene glycols; glycerin; polyether alcohols, such as DOWANOL™ TPM tripropylene glycol methyl ether, DOWANOL™ TPnB tripropylene glycol n-butyl ether, and DOWANOL™ PPH propylene glycol phenyl ether (available from The Dow Chemical Company); TRITON™ X-100 surfactant (available from Union  
10 Carbide); TERGITOL™ 15-S-9 ethoxylated surfactant (available from Union Carbide); and nonionic surfactants having an HLB value of at least 7.

When used, the dedusting agent will preferably be provided in an amount from 100 ppm to 5000 ppm by weight, more preferably in an amount from 300 to 3000 ppm by weight, based on the weight of the polymer particles. The dedusting agent may be applied  
15 through some form of mechanical distribution, such that adequate distribution of the dedusting agent on the aqueous fluid absorbent polymer particles occurs. Examples of blending equipment/processes include simple tumbling of a jar, or blending in a conical dryer, ribbon blender or drum tumbler. Moderate stirring, shaking, or even a short distance of conveying in a screw-conveyer can be sufficient for such adequate distribution of the dedusting  
20 agent over the particles, particularly if the particles are at a temperature greater than an ambient temperature.

While described in terms of gel polymerization technology, it is further possible to carry out the polymerization process using multi-phase polymerization processing techniques such as inverse emulsion polymerization or inverse suspension polymerization  
25 procedures. In the inverse emulsion polymerization or inverse suspension polymerization procedures, the aqueous reaction mixture as hereinbefore described is suspended in the form of tiny droplets in a matrix of a water-immiscible, inert organic solvent such as cyclohexane or ISOPAR™ mixed hydrocarbon (available from Exxon). Inverse emulsion polymerization and inverse suspension polymerization processes are sometimes advantageous, in that their use  
30 may enable better control of the exothermic heat of polymerization, and provide the flexibility of adding one or more of the aqueous reaction mixture components in a controlled manner to the organic phase.

Inverse suspension polymerization procedures are described in greater detail in U.S. Patent Nos. 4,340,706 and 4,506,052 and in PCT Patent Application 92/07336. When  
35 inverse suspension polymerization or inverse emulsion polymerization techniques are employed, additional ingredients such as surfactants, emulsifiers and polymerization stabilizers may be added to the overall reaction mixture. For instance, U.S. Patent Nos. 4,708,997 and

4,833,198, disclose a preferred stabilizer comprising a mixture of a copolymer of lauryl methacrylate and acrylic acid with silica and its use in suspension polymerization processes.

When any process employing organic solvent is utilized, the aqueous fluid absorbent polymer material will be treated to remove substantially all of the excess organic solvent. Preferably, the aqueous fluid absorbent polymers will contain no more than about 0.5 weight percent residual organic solvent.

The water-absorbent resin particles of this invention can be used in any use wherein absorption and binding of aqueous based fluids is desired. In a preferred embodiment, the water absorbent resin particles of this invention are mixed into or attached to a structure of absorbent material such as synthetic or natural fibers or paper-based woven or nonwoven fibers to form a structure. In such a structure the woven or nonwoven structure functions as a mechanism for wicking and transporting, via capillary action, the fluid to the water-absorbent resin particles which bind and retain such fluids. Such absorbent structures are typically employed in absorbent articles, such as diapers, adult incontinence structures and sanitary napkins.

Typical absorbent articles comprise a liquid-impermeable backing material, a liquid-permeable facing material, and an absorbent structure sandwiched therebetween. The absorbent structure will typically include a fibrous matrix, such as an air-laid batt of fluff, such as is formed according to the teachings of Mazurak and Fries as set forth in U.S. Patent No. 4,381,782. Suitable fibers for use in such a fibrous matrix include comminuted wood pulp, cotton linters, and melt-blown synthetic fibers such as polyethylene, polypropylene, polyesters, copolymers of polyesters and polyamides. The absorbent structure will typically comprise from 5 to 90 weight percent of the aqueous fluid absorbent material of the invention, with the balance of the absorbent structure comprising the fibrous matrix. U.S. Patent No. 5,147,343, provides one absorbent structure which exhibits low leakage. Accordingly, in one preferred embodiment of the absorbent structure of the invention, the aqueous fluid absorbent particles will have a size such that when wet, their diameter exceeds the median pore size of the porous fiber matrix. Particle diameters greater than 100 microns, more preferably greater than 150 microns, are most appropriate.

The following examples are included to illustrate the invention, and do not limit the scope of the claims. Unless otherwise stated, all parts and percentages are by weight. Unless otherwise stated, 60 minute 0.3 psi (21,000 dynes/cm<sup>2</sup>) AUL is measured as described in U.S. Patent No. 5,147,343, with 60 minute 0.6 psi (42,000 dynes/cm<sup>2</sup>) and 60 minute 1.0 psi (70,000 dynes/cm<sup>2</sup>) AUL being similarly measured with the test time and pressure being so adjusted; centrifuge capacity is determined as described in U.S. Patent No. 4,286,082 except that an absorption time of 30 minutes rather than 3 to 5 minutes is employed; the 16 hours extractables level is determined as described in U.S. Reissue Patent 32,649; and the residual monomer level is determined as described in GB 9,304,857 filed March 10, 1993.

ExamplesResin Preparation Procedure

Samples were prepared in a 200 L polymerization reactor with a stainless steel agitator assembly and a high torque stirring motor with gear reducers. The assembly allowed grinding of the gel formed during polymerization. The jacket was hollow and allowed heating or cooling of the reactor content by using a separate water circulating temperature device. The reactor was sealed and connected to a vacuum system, by which it was possible to cool the gel mass by pulling a vacuum.

In a separate vessel, 37.2 kg acrylic acid were added slowly to a mixture of 40.1 kg of an aqueous 50 percent solution of sodium hydroxide and 77 kg process water in such a way to prevent the temperature from rising above 38°C, to form a premix. To the premix, 70 g of a solution of a 40 weight percent active solution of VERSENEX™ 80 diethylene triamine pentaacetate chelating agent (trademark of The Dow Chemical Company) and 13 g partially hydrolyzed polyvinyl alcohol, dissolved in 130 mL pure water, were added and the premix was cooled to room temperature. The type and level of crosslinker indicated in Table I was added to 15.9 kg pure acrylic acid and the obtained mixture was added to the cooled premix. To the resultant mixture, optionally 305 ppmw potassium chlorate, based on the weight of the acrylic acid monomer was added to form a monomer mixture.

The prepared monomer mixture was pumped into the reactor, while purging with nitrogen. Via syringe, 900 g of a 10 percent aqueous sodium peroxodisulfate solution and 68 g of 30 weight percent active hydrogen peroxide were added to the reactor. A vacuum was pulled twice, in order to remove oxygen. The reactor headspace was filled with nitrogen. Reaction was initiated by the addition of 8 g ascorbic acid in 80 mL water. At the onset of polymerization, the external heater was set to 70°C. After the reaction reaches peak temperature (approximately 80°C), the reactor was cooled to 70°C by pulling vacuum. The gel was kept in the reactor for one hour at 70°C, removed from the reactor, minced, and dried in a belt drier for 20 minutes with an air stream at 170°C. A portion of the resulting dry product was ground in a lab mill, and was then screened to a 30 to 50 mesh cut.

The data set forth in Table I provides the resin formulations utilized in the various experiments, with the properties prior to heat-treatment as provided.

TABLE I  
Resin Formulations and Properties Prior to Heat-Treatment

Experiment No.	Crosslinker type	Crosslinker amount (ppmw)	Chlorate amount (ppmw)	Centrifuge Capacity	0.3 psi AUL (g/g)	Extractables (%)	Residual monomer (ppm)
1	allyl methacrylate	4000	0	27.3	26.3	4.9	715
2	allyl methacrylate	3500	305	26.1	24.3	5.6	590
3	allyl methacrylate	3000	305	30.5	17.5	8.6	314
4	allyl methacrylate	4000	305	33.2	12.4	ND	ND
5	HE TMPTA	4000	305	37.3	9.7	12.5	311
6	HE TMPTA	3000	305	40.9	9.7	14.7	335
7	HE TMPTA	3000	0	36	8.7	10.0	497
8	HE TMPTA	8000	305	31.5	21.6	6.8	463
9	HE TMPTA			37.3	10.7	11.7	335
10	HE TMPTA			40.0	11.5	14.1	303

Inhibitor Addition and Distribution Procedure 1:

0.5 kg of dry aqueous fluid absorbent polymer, as described in Table I, was placed into a horizontal blender which had a total volume of 3.2 L, which was jacketed for heating and cooling and which was equipped with a shaft carrying suitable mixing devices, a vacuum and condensation unit, and an injection line having an inner diameter of 3 mm. The product was heated to 120°C, while it was continually mixed at 38 rpm. In a separate beaker, 1 g of the desired inhibitor (2000 ppmw based on dry polymer) was dissolved in 75 mL water, with, in the case of gallic acid propionic ester (GAPE) the water having been heated to a temperature of 70°C to fully dissolve the inhibitor. The inhibitor solution was slowly injected via syringe on top of the product in the closed blender. The water component of the inhibitor solution was immediately evaporated, building up a relevant pressure within the closed blender. After the addition of the inhibitor solution, the product was held for 45 minutes at 120°C, while mixing was continued to distribute the inhibitor and permit its diffusion into the cores of the particles. Excess water was then removed by a 2 to 5 minute evacuation to 50 mbar. The product was then cooled to 40°C, and was removed from the blender.

Inhibitor Addition and Distribution Procedure 2:

50 g of dry aqueous fluid absorbent polymer, as described in Table I, was mixed in a glass bottle with a solution of 50 mg of the desired inhibitor, 4 g of isopropanol, and 2 g of standard room temperature water, with the aid of a spatula. The resultant mixture was mixed on a roller machine for 15 minutes.

Inhibitor Addition and Distribution Procedure 3:

50 g of dry aqueous fluid absorbent polymer, as described in Table I, was mixed in a glass bottle with a solution of the amount of gallic acid propyl ester (GAPE) inhibitor indicated in Table V, 4 g of isopropanol, and 3.75 g of standard room temperature water, and 50 mg of a polyoxyethylene-(2)-sorbitol lanoline derivative sold under the designation G-1425 by ICI Specialty Chemicals Goldschmidtstrasse 100, Essen, Germany, with the aid of a spatula. The resultant mixture was mixed on a roller machine for 15 minutes.

Inhibitor Addition and Distribution Procedure 4:

Hydrogel was produced using the standard recipe and polymerization procedure and using 5800 ppm of HE-TMPTA and 265 ppm of chlorate. After polymerization, the gel was chopped. One (1) kg of the chopped gel, while still at a temperature of preferably above 50°C, was mixed with a solution consisting of the relevant amount of GAPE, 70 mL of water, 30 mL of isopropanol and 2000 ppmw of a polyoxyethylene-(2)-sorbitol lanoline derivative sold under the designation G-1425 by ICI Specialty Chemicals, based on the total weight of the hydrogel. The such treated hydrogel was subsequently dried on a conveyor belt at 170°C.

Heat-Treatment Procedure:

A zone was preheated with a hot air gun. Once the target temperature indicated in Tables II, III, IV, and V was achieved and stabilized, the sample was placed in the zone. A

contact thermometer was placed in contact with the sample. The temperature of the sample was monitored until it stabilized at the target temperature. The sample was maintained at the target temperature for the time indicated in Tables II, III, IV, and V.

The data set forth in Table II pertained to the use of methoxy hydroquinone (MEHQ) as the inhibitor, as applied using Inhibitor Addition and Distribution Procedure 1, wherein the inhibitor was more homogeneously present in the polymer particles. The data set forth in Table III pertained to the use of gallic acid propyl ether (GAPE) as the inhibitor, as applied using Inhibitor Addition and Distribution Procedure 1, wherein the inhibitor was more homogeneously present in the polymer particles. The data set forth in Table IV pertained to the use of gallic acid propyl ester (GAPE) as the inhibitor, as applied using Inhibitor Addition and Distribution Procedure 2, wherein the inhibitor was more highly concentrated at the surface of the polymer particles. The data set forth in Table V pertained to the use of gallic acid propyl ester (GAPE) as the inhibitor, as applied using Inhibitor Addition and Distribution Procedure 3, wherein the GAPE was more highly concentrated at the surface of the polymer particles, and wherein the amount of GAPE was varied. The data set forth in Table VI pertained to the use of GAPE as the inhibitor, as applied to the Inhibitor Addition and Distribution Procedure 4, wherein the inhibitor was added to the hydrogel prior to gel drying.

20

25

30

35

TABLE II  
2000 ppmw MEHQ Inhibitor (based on polymer weight) as applied using  
Inhibitor Addition and Distribution Procedure 1.

Sample	Heat-treat conditions (°C/min.)	Centrifuge capacity (g/g)	0.3 psi AUL (g/g)	0.6 psi AUL (g/g)	1.0 psi AUL (g/g)	Extractables (%)	Residual Monomer (ppm)
1-Control*	200/10	30.9	29.4	12.7	9.1	4.8	781
1a	200/10	28.8	28.7	25.6	17.8	4.8	648
1b	210/10	29.3	28.6	25.5	16.0	4.9	743
1c	220/10	28.7	27.5	25.3	20.6	4.6	758
5-control*	200/10	38.9	30.3	11.9	8.3	9.7	395
5a	200/10	37.0	30.6	20.7	9.9	11.0	251
5b	210/10	37.0	30.3	22.2	12.2	10.7	299
5c	220/10	36.9	31.2	24.6	15.3	12.4	253
7-control-1*	200/5	31.1	29.5	17.4	9.1	7.8	503
7a	200/5	25.2	26.0	23.0	20.5	3.9	453
7-control-2*	220/15	27.7	27.7	24.3	12.4	6.1	563
7b	220/15	21.9	23.5	20.4	18.2	2.4	488

\*In the various controls, no MEHQ is utilized



TABLE III  
2000 ppmw GAPE Inhibitor (based on polymer weight) as applied using Inhibitor Addition and Distribution Procedure 1

Experiment No.	Heat-treat conditions (°C/min.)	Centrifuge capacity (g/g)	0.3 psi AUL (g/g)	0.6 psi AUL (g/g)	1.0 psi AUL (g/g)	Extractables (%)	Residual monomer (ppm)
1-control*	200/10	30.9	29.4	12.7	9.1	4.8	781
1d	200/10	28.3	28.7	25.7	21.2	4.7	651
1e	210/10	28.2	28.0	25.3	21.0	4.1	694
1f	220/10	27.5	27.3	24.9	22.3	3.6	758
4-control*	200/10	34.6	28.2	10.7	7.7	9.7	555
4d	200/10	31.5	30.4	25.2	18.6	7.1	432
4e	210/10	31.3	30.7	25.9	21.6	6.6	412
4f	220/10	30.7	29.8	26.1	23.1	7.1	380
5-control*	200/10	38.9	30.3	11.9	8.3	9.7	395
5d	200/10	32.7	31.1	25.2	15.2	7.0	491
5e	210/10	32.0	31.1	26.0	20.7	6.3	458
5f	220/5	32.8	30.5	26.3	19.9	7.2	418
5g	220/8	31.2	29.5	26.8	22.0	6.7	428
5h	220/10	30.6	29.8	26.3	22.4	6.8	420
5i	220/15	29.9	29.1	25.6	22.7	6.6	418
5j	220/20	29.3	27.5	25.3	22.4	7.2	380

\*In the various controls, no GAPE is utilized

TABLE IV  
1000 ppmw GAPE Inhibitor (based on polymer weight) as applied using Inhibitor Addition and Distribution Procedure 2

Experiment No.	Heat-treat conditions (°C/min.)	Centrifuge capacity (g/g)	0.3 psi AUL (g/g)	0.6 psi AUL (g/g)	1.0 psi AUL (g/g)	Extractables (%)	Residual monomer (ppm)
2a	210/15	37.4	32.5	25.4	14.6	17.9	611
3a	210/15	32.9	32.9	25.5	19.8	11.4	388
5-control*	200/10	38.9	30.3	11.9	8.3	9.7	395
5k	220/5	37.9	35.4	28.1	17.5	11.0	427
5l	220/8	36.8	34.4	29.2	22.4	10.3	344
5m	220/10	34.6	34.0	28.2	22.6	10.3	346
5n	220/15	34.0	32.1	27.1	22.1	12.0	317
5o	220/20	32.3	30.9	25.8	20.9	14.2	292
5p	230/8	36.4	34.7	28.1	23.7	13.2	389
8a	220/8	31.0	31.0	26.8	23.0	6.0	361
8b	230/8	31.8	31.9	26.5	23.2	6.8	350

\*In the control, no GAPE is utilized

TABLE :V  
GAPE Inhibitor Applied using Inhibitor Addition and Distribution Procedure 3

Sample	Heat-treat conditions (°C/min.)	GAPE concentration (ppm based on polymer)	Centrifuge capacity (g/g)	0.3 psi AUL (g/g)	0.6 psi AUL (g/g)	1.0 psi AUL (g/g)	Extractables (%)	Residual monomer (ppm)
6-control*	220/8	0	41.6	28.3	11.8	7.9	13.1	483
6a	220/8	50	36.2	34.9	30.0	25.2	19.6	436
6b	220/8	100	35.8	34.6	30.4	24.8	20.0	436
6c	220/5	200	38.4	36.6	30.5	25.2	17.1	456
6d	220/8	200	35.6	35.6	30.3	25.5	17.3	462
6e	220/10	200	35.3	35.5	29.7	25.9	17.3	453
6f	220/15	200	34.2	33.9	28.9	25.7	16.4	429
6g	220/20	200	32.5	32.6	28.7	25.1	15.5	400
6h	220/8	500	36.2	35.5	30.0	25.4	16.9	448
6i	220/8	2000	36.4	34.2	28.5	23.8	18.7	457
6j	220/8	5000	36.1	33.4	27.4	22.5	18.2	461

\*In the control, no GAPE is utilized

TABLE VI  
GAPE Inhibitor Applied using Inhibitor Addition and Distribution Procedure 4

Sample	Heat-treat conditions (°C/min.)	GAPE concentration (ppm based on polymer)	G1425 (ppm based on gel)	Centrifuge capacity (g/g)	0.3 psi AUL (g/g)	0.6 psi AUL (g/g)	1.0 psi AUL (g/g)	Extractables (%)	Residual monomer (ppm)
9-control-1	none	none	2000	37.3	10.7	8.0	ND	11.7	335
9-control-2	none	1000	2000	36.6	12.5	8.7	ND	11.3	236
9-control-3	none	2000	2000	36.8	15.2	7.4	ND	11.6	296
9-control-4	none	5000	2000	36.3	12.2	8.6	ND	11.6	296
9-control-5	210/20	none	2000	40.0	32.4	21.4	11.1	13.4	355
9a	210/20	1000	2000	34.6	31.5	25.7	14.8	10.9	407
9b	210/20	2000	2000	32.5	30.4	23.8	16.6	9.3	493
9c	210/20	5000	2000	32.4	30.3	25.9	15.6	9.3	546
10-control-1	none	none	none	40.0	11.5	8.3	ND	14.1	303
10-control-2	none	1000	none	37.3	19.7	8.9	ND	11.4	350
10-control-3	none	2000	none	35.3	13.4	8.5	ND	9.4	292
10-control-4	none	5000	none	33.8	14.7	8.6	ND	8.7	349
10-control-5	210/20	none	none	37.9	32.2	21.8	11.1	14.2	387
10a	210/20	1000	none	32.9	30.2	24.3	13.9	9.0	467
10b	210/20	2000	none	30.9	29.7	25.4	15.8	8.0	561

TABLE VI  
GAPE Inhibitor Applied using Inhibitor Addition and Distribution Procedure 4

Sample	Heat-treat conditions (°C/min.)	GAPE concentra- tion (ppm based on polymer)	G1425 (ppm based on gel)	Centrifuge capacity (g/g)	0.3 psi AUL (g/g)	0.6 psi AUL (g/g)	1.0 psi AUL (g/g)	Extract- ables (%)	Residual monomer (ppm)
10c	210/20	5000	none	29.7	29.8	25.9	21.1	7.8	700

Other embodiments of the subject invention will be readily determined by one skill in the art. Accordingly, the scope of the invention shall be limited only by the following claims.

5

10

15

20

25

30

35

## CLAIMS

1. An aqueous fluid absorbent polymer comprising the polymerization product of an ethylenically unsaturated monomer and optionally a comonomer copolymerizable with the ethylenically unsaturated monomer, the aqueous fluid absorbent polymer being crosslinked by a crosslinking agent having at least two moieties which react with the ethylenically unsaturated monomer and optionally the comonomer, wherein the aqueous fluid absorbent polymer is characterized by a centrifuge capacity of at least 25 grams/gram, and an absorption under a 1.0 psi (70,000 dynes/cm<sup>2</sup>) load of at least 15 grams/gram.

2. An aqueous fluid absorbent polymer of Claim 1, wherein the aqueous fluid absorbent polymer is further characterized by a level of extractable polymer less than 18 percent.

3. An aqueous fluid absorbent polymer of Claim 1, wherein the aqueous fluid absorbent polymer is characterized by a centrifuge capacity of at least 30 grams/gram, and an absorption under a 1.0 psi (70,000 dynes/cm<sup>2</sup>) load of at least 20 grams/gram.

4. An aqueous fluid absorbent polymer of Claim 1, wherein the aqueous fluid absorbent polymer is characterized by a centrifuge capacity of at least 35 grams/gram, and an absorption under a 1.0 psi (70,000 dynes/cm<sup>2</sup>) load of at least 25 grams/gram.

5. An aqueous fluid absorbent polymer of Claim 1, wherein the aqueous fluid absorbent polymer is characterized by the residue of an inhibitor in an amount of from 10 to 5000 ppmw based on the weight of the polymer and residue of an inhibitor.

6. A process for preparing an aqueous fluid absorbent polymer comprising:

- (a) polymerizing an ethylenically unsaturated monomer and optional comonomer copolymerizable with the ethylenically unsaturated monomer, in the presence of a crosslinking agent having at least two moieties which react with the ethylenically unsaturated monomer and optionally the comonomer, to form aqueous fluid absorbent beads or a hydrogel;
- (b) removing solvent from the aqueous fluid absorbent beads or water from the hydrogel to form a dried aqueous fluid absorbent polymer material; and
- (c) heat-treating the dried aqueous fluid absorbent polymer material at a temperature from 180°C to 240°C to form a heat-treated aqueous fluid absorbent polymer material;

wherein the dried aqueous fluid absorbent polymer material contains an inhibitor during the heat-treating of step (c), the inhibitor being provided subsequent to the polymerizing of step (a) and prior to the heat-treating of step (c).

7. A process of Claim 6, wherein the inhibitor is substantially homogeneously present in the dried aqueous fluid absorbent polymer material during the heat-treating of step (c).
8. The process of Claim 7, wherein the inhibitor is provided in an amount from 100 to 5000 ppmw, based on the weight of the dried aqueous fluid absorbent polymer material.
9. A process of Claim 6, wherein the inhibitor is more highly concentrated at the particle surfaces of the dried aqueous fluid absorbent polymer material during the heat-treating of step (c).
10. A process of Claim 9, wherein the inhibitor is present in the dried aqueous fluid absorbent polymer material in an amount of from 25 ppmw to 8,000 ppmw, based on the weight of the dried aqueous fluid absorbent polymer material.
11. A process of Claim 9, wherein the inhibitor is present in the dried aqueous fluid absorbent polymer material in an amount of from 25 ppmw to 500 ppmw, based on the weight of the dried aqueous fluid absorbent polymer material.
12. A process of Claim 6, wherein the inhibitor is applied to the hydrogel prior to the removing of step (b).
13. A process of Claim 12, wherein the inhibitor is provided in an amount from 1,000 to 10,000 ppmw, based on the weight of the aqueous fluid absorbent beads or hydrogel.
14. A process of Claim 6, wherein the inhibitor is sulfites, phenols, aromatic amines, organo sulfur compounds, phosphorus compounds or hindered amines, ascorbic acid or its derivatives, gallic acid or its derivatives, benzothiazoles, dithionates, thiurams, benzimidazoles, formaldehyde sulfoxylates or phenothiazines.
15. A process of Claim 6, wherein the inhibitor is gallic acid or its derivatives, quinone or its derivatives or hydroquinone or its derivatives.
16. A process of Claim 6, wherein the inhibitor is gallic acid propyl ester.
17. A process of Claim 6, wherein the crosslinking agent is highly ethoxylated trimethylol propane triacrylate, the inhibitor is gallic acid propyl ester, or methoxy hydroquinone, and optionally wherein a chlorate or bromate salt is provided to the dried aqueous fluid absorbent polymer material subsequent to the polymerizing of step (a) and prior to the heat-treating of step (c).
18. A process of Claim 6, wherein the crosslinking agent is allyl methacrylate; the inhibitor is gallic acid propyl ester or methoxy hydroquinone; and optionally, when the inhibitor is gallic acid propyl ester, wherein a chlorate or bromate salt is provided to the dried aqueous fluid absorbent material subsequent to the polymerizing of step (a) and prior to the heat-treating of step (c).



## INTERNATIONAL SEARCH REPORT

Inter nal Application No

PCT/US 94/09665

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 A61L15/00 C08F2/32 C08F8/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61L C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO,A,93 05080 (THE DOW CHEMICAL COMPANY) 18 March 1993 cited in the application see claims 1-23 ---	1-21
Y	EP,A,0 259 037 (KAO CORPORATION) 9 March 1988 see page 3, line 1 - line 28; claims 1-6 ---	1-21
Y	EP,A,0 249 391 (SEITETSU KAGAKU CO., LTD.) 16 December 1987 see claims 1-8 ---	1-21
A	US,H,B494440 (J. R. GROSS) 17 February 1976 see claims 1-13 --- -/--	1



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*&\* document member of the same patent family

Date of the actual completion of the international search

2 November 1994

Date of mailing of the international search report

11. 11. 94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+ 31-70) 340-3016

Authorized officer

Permentier, W

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 94/09665

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EP,A,0 240 586 (GREGOR, HARRY P.) 14 October 1987 see claims 1-16</p> <p>-----</p>	1

# INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No  
PCT/US 94/09665

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9305080	18-03-93	AU-A- 2590592 CA-A- 2116035 EP-A- 0603292	05-04-93 18-03-93 29-06-94
EP-A-0259037	09-03-88	JP-A- 63152667 US-A- 4812486	25-06-88 14-03-89
EP-A-0249391	16-12-87	CA-A- 1330868 DE-A- 3778429 US-A- 4863989 US-A- 4972019 JP-B- 5034383 JP-A- 63118375	26-07-94 27-05-92 05-09-89 20-11-90 21-05-93 23-05-88
US-H-B494440	17-02-76	US-A- 4056502	01-11-77
EP-A-0240586	14-10-87	US-A- 4596858	24-06-86